Indian J. Phys. **68A** (2), 173–181 (1994)

I J P A
- an international journal

Temperature dependence of thermal expansivity for alkali halides

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Received 22 June 1993, accepted 8 November 1993

Abstract : In the present paper, we develop a simple method to investigate the thermal expansion coefficient of sixteen NaCl type alkali halide crystals as a function of temperature starting from room temperature upto nearly the melting temperature A simple formula is derived by assuming that the Anderson parameter remains constant under the effect of high temperature An isobaric equation of state based on the quantum mechanical Harrison's overlap repulsive potential is used to estimate the values of interatomic separations corresponding to different temperatures. The results are compared with the available experimental data and are discussed in the light of recent research in the field of high temperature physics A rather fast increase in the thermal expansion coefficient with temperature as consistent with physical grounds is obtained.

Keywords : Alkali halide crystals, thermal expansivity, interatomic separation

PACS No. : 65 70 +y

1. Introduction

Various efforts have been made to study the thermal expansion of ionic solids [1-6]. Among the several available experimental data, only three have been employed [7-9], to determine and discuss the temperature dependence of volume thermal expansion coefficient (α). Spetzler *et al* [7] have determined the thermal expansion data for NaCl by evaluating the ultrasonic frequencies as a function of temperature and pressure. The random errors were corrected by fitting the data with a polynomial expression in temperature and pressure. Srivastava and Merchant (henceforth to be referred as SM) [8] investigated the thermal expansion through the equation of state by measuring the lattice parameters for nine alkali halides with NaCl structure from room temperature to nearly melting temperature using X-ray diffractometric technique. A quadratic equation with least square error approximation was fitted to the lattice parameter *versus* temperature data. Boyer [9] has analysed the thermal

expansion data of several workers and has shown that the best fit with the higher temperature data is obtained through an equation of the form

$$a(T) = a(T_c) - a_1(T_c - T)^{1/2}$$

where a_1 is a positive constant, T_c is a critical temperature assumed to be equal to or close to the melting temperature T_m, and a (T) is the linear dimension of the crystal at temperature T. These methods have been analysed critically by Dhoble and Verma [10] for the calculation of temperature dependence of α. It should be pointed out that both Spetzler *et al* (at zero pressure) and SM have fitted their thermal expansion data by a quadratic function of temperature. It is obvious that a quadratic expression for temperature with lattice parameter will give a linear variation of α with temperature. It is however, an acceptable fact on the physical ground that α must become rather large ($\alpha \to \infty$ as $T \to T_m$) as discussed in detail by Shanker and Kumar [11]. Therefore, the slow variation of α reported by the authors [7,8] needs further investigation.

On the basis of thermodynamic analysis [12], α can be related to the density of crystal assuming that the isothermal Anderson parameter is independent of temperature. A number of experimental results have demonstrated the validity of this assumption as discussed in detail by Anderson and coworkers [12,13]. The purpose of the present work is to demonstrate that this assumption leads to a simple relation for determining the variation of thermal expansion coefficient with temperature. It is further shown that the results obtained from the relation thus derived, are more consistent with the physical grounds [11]. The calculations require the interatomic separations as a function of temperature which are obtained from isobaric equation of state based on the quantum-mechanical Harrison's overlap repulsive potential, as recently developed by Sherry and Kumar [14]. The method of analysis is described in Section 2. Results are discussed and compared with the available experimental data in Section 3.

2. Method of analysis

A useful quantity for the discussion of anharmonic properties of solids is the Anderson parameter which is defined as [15,16].

$$\delta_T = -\frac{1}{\alpha B_T}\left[\frac{\partial B_T}{\partial T}\right]_P \tag{1}$$

where,

$$\alpha = \frac{1}{v}\left[\frac{\partial v}{\partial T}\right]_P \tag{2}$$

is the coefficient of thermal expansion and

$$B_T = -V\left[\frac{\partial P}{\partial V}\right]_T \tag{3}$$

is the isothermal bulk modulus. The well known Maxwell thermodynamic identity is,

$$B_T\left[\frac{\partial\alpha}{\partial P}\right]_T = \frac{1}{B_T}\left[\frac{\partial B_T}{\partial T}\right]_P. \tag{4}$$

Using eqs. (1), (3) and (4) we get

$$\frac{d\alpha}{\alpha} = \delta_T \frac{dV}{V}. \tag{5}$$

Integration of eq. (5) gives the following result

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0}\right)\delta_T \tag{6}$$

where α_0 and V_0 are the thermal expansion coefficient and volume referred to room temperature and atmospheric pressure ($P = 0$). For the solids with NaCl-type structure, $V = 2r^3$ where r is the interatomic separation. Thus, eq. (6) can be rewritten as

$$\frac{\alpha}{\alpha_0} = \left(\frac{r}{r_0}\right)3\delta_T. \tag{7}$$

It has been shown by Anderson and coworkers [12,13,15,17] that δ_T is independent of temperature. Anderson [12] presented the derivation of (6) in a slightly different form. He started with a thermodynamic identity given by (4) but changed the variable from P to V, resulting an equation which is equivalent to (5). It should be mentioned that Dass and Kumari [18] have also derived a relation similar to that of (6) [See eq. (11) of their paper] and showed that their formula is similar to that given by Anderson [15]. However, they have used some additional assumptions. Moreover, the final formula reported by Dass and Kumari [18] contains an error regarding the power of (V/V_0) which should be δ_T in the place of $1/\delta_T$. We make use of eq. (7) to calculate the values of α at different temperatures. For this purpose, we need the values of r at different temperatures, which are evaluated using the equation of state given below [14]

$$P = -\frac{dW}{dV} + T\alpha B_T. \tag{8}$$

For solids of NaCl type structure $V = 2r^3$ and therefore we can rewrite eq. (8) as follows :

$$P = -\frac{1}{6r^2}\frac{dW}{dr} + T\alpha B_T \tag{9}$$

where W is the crystal lattice energy and T is the temperature. At atmospheric pressure ($P = 0$) we obtain from eq. (9)

$$T = \frac{1}{6r^2\alpha B_T}\frac{dW}{dr}. \tag{10}$$

Eq. (10) has been used to calculate temperatures corresponding to different values of r by adopting some potential energy expression for W and assuming that the product (αB_T) remains unchanged under the effect of high temperature [11,14]. For an ionic solid, the lattice potential energy W can be written as follows [14] :

$$W = -\frac{\alpha_m e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + W_{rep} \tag{11}$$

where the first term of the right hand side is the Coulomb energy with α_m as Madelung's constant. The second and third terms are the *vdW* energies with C and D as dipole-dipole and dipole-quadrupole coefficients which are evaluated using Kirkwood-Muller formulae as discussed by Shanker and Agrawal [19]. W_{rep} is the overlap repulsive energy considered between nearest neighbours and next nearest neighbours. Using Harrison's potential form, we can write [11]

$$W_{rep} = \frac{6n_0\hbar^2}{2m}\left[\bar{\mu}^{-1} r \exp\left(-k\bar{\mu}r\right) + \sqrt{2}\,\mu_1^{-1} r \exp\left(-\sqrt{2}k\,\mu_1 r\right)\right.$$

$$\left. + \sqrt{2}\mu_2^{-1} r \exp\left(-\sqrt{2}\,k\mu_2 r\right)\right], \tag{12}$$

where $\hbar$ is Planck's constant divided by 2π and m the mass of electron. $\bar{\mu}$ is the arithmatic average of μ_1 and μ_2 for cation and anion, respectively. Values of μ_1 and μ_2 can be calculated by the relation [11]

$$\mu_i^2 = -\frac{2m\varepsilon_i}{\hbar^2}, \tag{13}$$

where ε_i is the valence state energy. The potential parameters n_0 and k have been calculated using the following relations

$$\left(\frac{dW}{dr}\right)_{r=r_0} = 0, \tag{14}$$

$$\left(\frac{d^2W}{dr^2}\right)_{r=r_0} = 18 r_0 B_T, \tag{15}$$

where B_T is the isothermal bulk modulus and r_0 is the value of r at $T = 0K$. The potential parameters thus calculated are considered to be independent of temperature. Using these parameters we have calculated the values of dW/dr at different values of r, and corresponding temperature is evaluated from eq. (10). Thus, we have performed the calculations of r *versus* T such that the maximum temperature achieved is less than the melting temperature in each case. Using these values of r at different T we have evaluated α from eq. (7). The

experimental values of δ_T derived from thermoelastic data [20] are given in Table 1, alongwith the values of α_0 and r_0. The results thus obtained are given in Table 2.

Table 1. Values of input parameter [10, 20].

Crystal	$\alpha_0 (10^{-4} K^{-1})$	r_0 (Å)	δ_T
LiF	0.999	2.013	6.00
LiCl	1.32	2.570	6.77
LiBr	1.50	2.751	7 01
LiI	1.80	3.006	7 32
NaF	0.96	2.317	5.77
NaCl	1.19	2.820	5 85
NaBr	1.26	2.989	6.23
NaI	1.37	3.236	6.43
KF	1.02	2 674	6.20
KCl	1.11	3.146	6.22
KBr	1.16	3.300	5.88
KI	1.23	3.533	5 76
RbF	0 94	2.826	6.80
RbCl	1.03	3 291	6 76
RbBr	1.08	3.445	6.60
RbI	1.23	3 671	6.52

3. Results and discussions

We have thus estimated the temperature dependence of α from room temperature upto the temperature approaching the melting point such that the last temperature entered is less than the melting temperature. The calculations of α performed in the present work are based on the assumption that δ_T is independent of T. It should be mentioned that Dhoble and Verma [10] studied the case of only NaCl at 300 K, 550 K and 800 K and predicted a slight variation of δ_T with temperature. However, a recent detailed analysis performed by Anderson and coworkers [17,21,22] demonstrates that δ_T is very nearly independent of T above Debye temperature θ but not below θ. Since for the solids considered in present work, the room temperature is above θ, we can therefore safely use this approximation. Boehler *et al* [23] and Chopelas [24] also demonstrated that δ_T is independent of V for several important minirals. Chopelas and Boehlar [25] demonstrated the validity of this approximation for alkali metals. Thus approximation 'δ_T independent of T' used in the present work, is not new but already used by several investigations.

The results obtained in the present study are compared with the available experimental data of SM [8]. It is seen from Table 2 that the rate of variation of α with T predicted from

Table 2. Values of thermal expansion coefficient α in (10^{-4} K^{-1}) alongwith the values of r(Å) and T(K). Calculated values of α are given in column (a) and those reported by SM [8] in (b).

LiF				LiCl			LiBr			LiI		
r	T	α		r	T	α	r	T	α	r	T	α
		(a)	(b)			(a)			(a)			(a)
2.013	298	0.999	0.975	2.570	298	1 32	2 751	298	1.50	3 006	298	1.80
2.02	350	1 06	1 04	2 58	350	1 43	2 76	350	1 61	3 04	390	2.30
2.04	625	1.27	1.41	2 60	430	1 67	2 78	472	1.87	3.06	470	2.66
2 06	850	1 51	1 72	2 62	560	1 95	2 80	590	2 17	3 08	560	3.07
2 08	1000	1 80	1 90	2.64	672	2 27	2 82	611	2 52	3 10	630	3.53
				2 66	805	2 65	2 84	728	2 93			
				2 67	880	2 86						

NaF				NaCl				NaBr			NaI		
r	T	α		r	T	α		r	T	α	r	T	α
		(a)	(b)			(a)	(b)			(a)			(a)
2 317	298	0 96	0.95	2.82	298	1 19	1 16	2 989	298	1 26	3 236	298	1.37
2 32	310	0 98	0 98	2 83	409	1 27	1 33	3 00	380	1 35	3 240	320	1.40
2.34	505	1.14	1.24	2.84	484	1 35	1 44	3.02	550	1 52	3 26	425	1.58
2.36	710	1.32	1.50	2 85	620	1.43	1.64	3.04	680	1 72	3.28	530	1.77
2.38	915	1.52	1.75	2.86	643	1.52	1.68	3.06	800	1 95	3 30	640	1.99
2.40	1018	1.76	1.85	2.88	786	1 72	1 90	3.08	910	2.20	3.32	738	2.24
2.42	1123	2.03	2.00	2.887	835	1 80	1.95	3 10	1011	2 49	3.34	820	2.52

Table 2. (*Contd*)

KF			KCl				KBr				KI			
r	*T*	α	*r*	*T*	α		*r*	*T*	α		*r*	*T*	α	
		(a)			(a)	(b)			(a)	(b)			(a)	(b)
2.674	298	1 02	3 146	298	1 11	1 11	3 300	298	1 16	1.24	3.533	298	1.23	1.17
2.68	370	1.06	3.16	341	1 20	1 09	3 32	503	1.29	1.29	3 54	348	1.27	1.23
2 70	524	1.22	3.18	490	1.35	1.24	3 34	647	1 43	1 40	3 56	463	1.40	1.36
2.72	710	1.40	3 20	640	1.52	1 40	3 36	776	1 59	1.53	3.58	568	1 54	1 40
2.74	970	1.60	3.22	775	1 71	1.53	3.38	894	1 76	1 63	3.60	665	1.70	1.47
2.76	1005	1.83	3.24	893	1 92	1.65					3 64	832	2.05	1 67

RbF			RbCl				RbBr				RbI			
r	*T*	α	*r*	*T*	α		*r*	*T*	α		*r*	*T*	α	
		(a)			(a)	(b)			(a)	(b)			(a)	(b)
2.826	298	0.94	3.291	298	1 03	1.10	3.445	298	1 08	1 13	3.671	298	1 23	1.16
2.84	430	1.03	3 32	418	1 23	1.26	3.46	325	1.15	3 15	3 70	400	1 43	1.25
2 86	542	1 19	3 34	530	1 38	1.32	3 48	415	1.31	1 20	3 72	469	1.59	1 30
2 88	659	1.38	3 36	628	1 56	1 37	3 50	505	1.47	1.24	3 74	541	1.77	1.36
2.90	783	1.59	3 38	750	1 76	1.44	3 52	691	1.65	1 34	3 76	611	1.96	1.42
2.92	901	1.83	3 40	876	1.99	1.51	3 54	780	1 85	1 39	3 78	782	2.18	1 56

both the studies differ appreciably from eachother. The increase of α with temperature predicted in the present study is, in general, significantly more rapid than that reported by SM. Dhoble and Verma [10] made a critical analysis of the results reported by SM and found some remarkable inconsistencies in their data. They concluded that α should increase more rapidly with temperature as compared to the variation shown by the results due to SM. This conclusion has also been supported by the work of Boyer [9] on thermal expansion of NaCl. Studies on melting as reviewed by Shanker and Kumar [11] have also revealed that α must increase rapidly tending towards ∞ as the melting temperature is approached. An interesting feature of the results obtained in present study is that α calculated at a temperature close to the melting temperature is found nearly double to that the room temperature value of α. Thus, the present conclusions are in good agreement with the recent research in the high temperature physics and the theories of melting [11].

Acknowledgment

The author is thankful to the referee for valuable comments which have been found very useful in revising the manuscript.

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